Chemistry of the Metal Carbonyls. Part LXIII.[1] New Cluster Carbonyl Compounds Containing Platinum and Iron

By M. I. Bruce, G. Shaw, and F. G. A. Stone,* Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Reactions between tertiary phosphine-, phosphite-, or arsine-platinum complexes and $Fe_2(CO)_9$ afford the cluster carbonyls $Fe_2Pt(CO)_9L$ (I) (L = PPh_3, PPh_2Me, $PPhMe_2$, PMe_3, or $AsPh_3$) and $Fe_2Pt(CO)_8L_2$ (II) [L = PPh_3, PPh_2Me, $PPhMe_2$, PMe_3, $PPh(OMe)_2$, or $P(OPh)_3$; L_2 = diphos or diars]. I.r. and ^1H n.m.r. spectra are discussed, and these enable possible structures to be proposed.

THERE has been much recent interest in homonuclear cluster compounds containing platinum. The complexes $[Pt(PPh_3)]_4$ and $[Pt(PPh_3)_2]_3$ are thought [2,3] to contain respectively tetrahedral and triangular clusters of platinum atoms. More recently, the preparation of various tri- and tetra-nuclear platinum complexes containing tertiary phosphines or arsines, as well as carbonyl groups as ligands, has been described.[4] The structure of one of these compounds, $Pt_4(CO)_5(PPhMe_2)_4$, has been determined by *X*-ray crystallography.[5]

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[1] Part LXII, A. Brookes, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 3469.

[2] A. J. Layton, R. S. Nyholm, G. A. Pneumaticakis, and M. L. Tobe, *Chem. and Ind.*, 1967, 465.

[3] R. D. Gillard, R. Ugo, F. Cariati, S. Cenini, and F. Bonati, *Chem. Comm.*, 1966, 869.

[4] J. Chatt and P. Chini, *J. Chem. Soc.* (*A*), 1970, 1538.

[5] R. G. Vranka, L. F. Dahl, P. Chini, and J. Chatt, *J. Amer. Chem. Soc.*, 1969, **91**, 1574.

Complexes containing platinum bonded to other Group VIII metals *via* discrete Pt–Fe,[6] Pt–Co,[7,8] and Pt–Ni[2] bonds have also been described, but heteronuclear cluster compounds containing platinum and these elements have hitherto remained unknown. Herein we report the syntheses and properties of several new cluster carbonyls containing platinum bonded to iron, and stabilised by the presence of a variety of tertiary phosphines, phosphites, or arsines.[9]

TABLE 1

Analytical[a] and physical data for some iron–platinum cluster compounds[b]

Compound	M.p.	% Yield	C	H	O	P or As	Fe	Pt	*M*
$Fe_2Pt(CO)_9(PPh_3)$	119—120°	16	39·6(39·5)	1·75(1·85)		3·9(3·75)	13·45(13·6)		790(821)
$Fe_2Pt(CO)_8(PPh_3)_2$	138—140	1·5	49·55(50·05)	2·80(2·85)					
$Fe_2Pt(CO)_8(PPh_2Me)_2$	140—142	23	43·8(43·85)	2·75(2·8)		6·6(6·65)	11·60(12·0)		810(931)
$Fe_2Pt(CO)_8(PPhMe_2)_2$	124—125	23	35·7(35·7)	3·15(2·75)	16·3(15·85)	7·65(7·65)	13·9(13·85)	24·40(24·15)	690(807)
$Fe_2Pt(CO)_8(PMe_3)_2$	121—124[d]	2·1	24·9(24·65)	2·6(2·65)					
$Fe_2Pt(CO)_8[PPh(OMe)_2]_2$	138—139	37	33·05(33·1)	2·55(2·55)	22·1(22·05)	6·7(7·1)	12·6(12·8)	22·40(22·40)	856(871)
$Fe_2Pt(CO)_8[P(OPh)_3]_2$	145—146	11	45·75(45·9)	2·6(2·65)	19·45(19·45)	5·4(5·4)	10·1(9·7)	17·70(16·95)	980(1151)
$FePt_2(CO)_5[P(OPh)_3]_3$[e]	145—146[d]	8·5	46·4(46·7)	2·95(3·0)	14·8(14·75)	6·05(6·15)	3·8(3·7)	25·80(25·70)	1486(1517)
$Fe_2Pt(CO)_8$(diphos)	196—198	5	43·65(43·95)	2·65(2·6)			11·8(12·0)		
$Fe_2Pt(CO)_8$(diars)	170—171	14	26·65(26·45)	1·95(2·0)		18·3(18·35)	13·85(13·65)		

[a] Calculated values given in parentheses. [b] Compounds deep red. [c] Determined in $CHCl_3$ using a Mechrolab osmometer. [d] With decomposition. [e] Orange in colour.

The reaction between $Pt(PPh_3)_4$ or $Pt(PPh_3)_2$ (*trans*-stilbene) and $Fe_2(CO)_9$ gave several complexes, which could be separated readily by chromatography. These were shown to be the known complexes $Fe(CO)_4(PPh_3)$ and $Fe(CO)_3(PPh_3)_2$ (identified by their solution infrared spectra), and air-stable deep red prisms with the stoicheiometry $Fe_2Pt(CO)_9(PPh_3)$ (I) (Table 1). The i.r. spectrum (Table 2) showed only terminal ν(CO) frequencies, and attempts to obtain the mass spectrum resulted in decomposition, only ions found in the spectrum of $Fe(CO)_4(PPh_3)$ being observed. An analogous complex was obtained from the reaction between $Pt(AsPh_3)_4$ and $Fe_2(CO)_9$, and this exhibited a similar ν(CO) spectrum. The n.m.r. spectra of both complexes showed only signals due to the phenyl resonances.

TABLE 2

Carbonyl stretching frequencies of iron–platinum cluster compounds

Complex	$\nu_{(CO)}$, cm^{-1} (cyclohexane)
$Fe_2Pt(CO)_9(AsPh_3)$[a]	2077s, 2034s, 2017s, 2007sh, 1989s, 1924w
$Fe_2Pt(CO)_9(PPh_3)$	2074s, 2035s, 2014s, 2001m, 1985s, 1973sh, 1924w,br
$Fe_2Pt(CO)_9(PPh_2Me)$	2075s, 2036s, 2013s, 1999sh, 1986s, 1969m, 1957sh, 1927w,br
$Fe_2Pt(CO)_9(PPhMe_2)$[a]	2074m, 2028s, 2012s, 1996sh, 1985s, 1968m, 1936w
$Fe_2Pt(CO)_9(PMe_3)$[a]	2076m, 2031s, 2012s, 2003sh, 1986s, 1970m, 1954sh, 1934w
$Fe_2Pt(CO)_8(PPh_3)_2$	2054s, 2006s, 1984sh, 1974m, 1956m, 1942sh, 1878w,br
$Fe_2Pt(CO)_8(PPh_2Me)_2$	2047s, 1999s, 1973m, 1951w, 1882w,br
$Fe_2Pt(CO)_8(PPhMe_2)_2$	2051s, 1998s, 1971m, 1948m, 1892w,br
$Fe_2Pt(CO)_8(PMe_3)_2$	2049s, 1993s, 1968s, 1945s, 1900w,br
$Fe_2Pt(CO)_8[PPh(OMe)_2]_2$	2057s, 2006s, 1977sh, 1967s, 1959sh, 1916w,br
$Fe_2Pt(CO)_8[P(OPh)_3]_2$	2073m, 2012s, 1992sh, 1983m, 1966m, 1926w,br
$FePt_2(CO)_5[P(OPh)_3]_3$	2032sh, 2015s, 1952m, 1918m
$Fe_2Pt(CO)_8$(diphos)	2053s, 2004s, 1971s, 1956m, 1916w,br
$Fe_2Pt(CO)_8$(diars)	2065s, 2003s, 1977s, 1949s, 1909w,br

[a] Identified only from i.r. spectrum.

Using other phosphorus ligands, a second series of compounds of stoicheiometry $Fe_2Pt(CO)_8L_2$ (II) was obtained, for $L = PMePh_2$, PMe_2Ph, $P(OPh)_3$, $PPh(OMe)_2$, and for $L_2 = Ph_2P(CH_2)_2PPh_2$ (diphos) or $o\text{-}C_6H_4(AsMe_2)_2$ (diars). These complexes are all air-stable and crystallise as deep red prisms. The carbonyl i.r. spectra are all similar, and indicate the presence of terminal carbonyl groups only.

TABLE 3

Proton n.m.r. data for some iron–platinum clusters[a]

Compound	τ Phenyl	τ CH_3P–Pt
$Fe_2Pt(CO)_9(PPh_3)$	2·58m	
$Fe_2Pt(CO)_8(PPh_3)_2$	2·66m	
$Fe_2Pt(CO)_9(PPh_2Me)$	3·04m	8·12d, $J_P = 10·75$ $J_{Pt} = 33·0$
$Fe_2Pt(CO)_8(PPh_2Me)_2$	2·82m	7·98d, $J_P = 9·5$ $J_{Pt} = 32·0$
$Fe_2Pt(CO)_8(PPhMe_2)_2$	2·65m	8·22d, $J_P = 10·5$ $J_{Pt} = 32·0$
$Fe_2Pt(CO)_8(PMe_3)_2$	—	8·23d, $J_P = 10·5$ $J_{Pt} = 32·0$
$Fe_2Pt(CO)_8[PPh(OMe)_2]_2$	2·62m	6·56d, $J_P = 12·75$
$Fe_2Pt(CO)_8[P(OPh)_3]_2$	2·90m	
$FePt_2(CO)_5[P(OPh)_3]_3$	2·95m	
$Fe_2Pt(CO)_8$(diphos)	2·51m	(CH_2, 7·83m)
$Fe_2Pt(CO)_8$(diars)	2·33m	8·10, $J_{Pt} = 20·50$

[a] In $CDCl_3$. [b] In C_6D_6.

The ^1H n.m.r. spectra of the $PMePh_2$ and PMe_2Ph complexes exhibited a triplet of apparent doublets, with relative intensities 1 : 4 : 1, for the methyl protons (Table 3). This pattern is characteristic[10] of two tertiary phosphine ligands co-ordinated in relative *cis*-positions to a platinum atom. In the case of the $PPh(OMe)_2$ complex, the splitting due to the ^{195}Pt nucleus was not found, although the methyl resonance

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[6] M. Akhtar and H. C. Clark, *J. Organometallic Chem.*, 1970, **22**, 233.

[7] R. G. Pearson and J. Dehand, *J. Organometallic Chem.*, 1969, **16**, 485.

[8] D. Moras, J. Dehand, and R. Weiss, *Compt. rend.*, 1968, **267***C*, 1471.

[9] M. I. Bruce, G. Shaw, and F. G. A. Stone, *Chem. Comm.*, 1971, 1288.

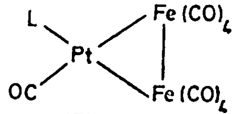
[10] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 770.

is a doublet due to phosphorus coupling. A similar spectrum was observed for the complexes *cis*-$PtX_2[P(OMe)_3]_2$.[11] The methylene protons in the chelated diphos derivative exhibit the complex pattern at τ 7·83, associated with compounds of this ligand.

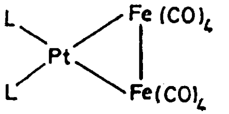
Treatment of *cis*-$PtCl_2(PMe_3)_2$ with $Fe_2(CO)_9$ in benzene–tetrahydrofuran solution afforded low yields of (I) and (II) ($L = PMe_3$). The former decomposed when set aside in air, and was identified by comparison of its i.r. spectrum with those of other similar complexes. Reactions between $Fe_2(CO)_9$ and $Pt(PMe_2Ph)_4$ gave (II; $L = PMe_2Ph$) as the only isolated product, although (I; $L = PMe_2Ph$) was detected spectroscopically in the reaction mixture. When a suspension of $Fe_2(CO)_9$ in a benzene solution of $Pt(PMePh_2)_4$ was refluxed for 2 h, no products other than (II; $L = PMePh_2$) were isolated. No iron–platinum cluster compounds could be isolated from the reaction between $Fe(CO)_5$ and $Pt(PMePh_2)_4$ in benzene.

Reaction of the olefin complex $Pt(PPh_3)_2$(*trans*-stilbene) with $Fe_3(CO)_{12}$ afforded both complexes (I) and (II) ($L = PPh_3$), together with two brownish red compounds. The i.r. spectra of these complexes are similar, and contain bands characteristic of both bridging and terminal carbonyl groups. Analytical data suggest the compositions $Pt_4(CO)_n(PPh_3)_3$ ($n = 6$ and 8, respectively).

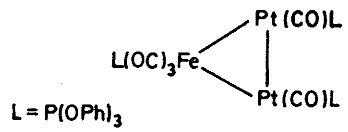
A reaction between $Fe_3(CO)_{12}$ and $Pt(PPh_2Me)_4$ afforded (II; $L = PPh_2Me$) and a third red-brown complex, which had an i.r. spectrum similar to those of the platinum complexes mentioned above. It was not further characterised.



(I)



(II)



(III)

Treatment of the iron–platinum cluster complexes with concentrated sulphuric acid resulted in rapid decomposition, and no complex hydrido-species could be detected by ^1H n.m.r. studies, even using freshly prepared, ice-cold solutions. Attempts to prepare analogous iron–palladium cluster compounds from reactions between $Fe_2(CO)_9$ and PdL_4 [$L = PPh_3$, $PMePh_2$, or $P(OPh)_3$] failed.

From the reaction between $Fe_2(CO)_9$ and $Pt[P(OPh)_3]_4$, a second and new type of complex was obtained in addition to [II; $L = P(OPh)_3$]. This formed air-stable orange prisms with the composition $FePt_2(CO)_5[P(OPh)_3]_3$ (III). The i.r. spectrum establishes the presence of only terminal carbonyl groups, and bands at 800 and 1100 cm^{-1}, characteristic [12] of *ortho*-metallated $P(OPh)_2(OC_6H_4)$ ligands, are absent from the spectrum. No high-field signal was found in the ^1H n.m.r. spectrum. The structure of this complex is not clear, but may be of the type shown in which one of the phosphite ligands has become attached to the iron atom. An *X*-ray crystallographic study is in progress.

The structures of complexes (I) * and (II) are assigned as shown. The number of ligands requires a triangular configuration of metal atoms, and the n.m.r. spectra of the appropriate phosphine-substituted complexes suggest that the phosphorus ligands remain bonded to platinum. As is now becoming a common feature of Group VIII cluster chemistry, these complexes are formally electron deficient in the sense that the effective atomic number formulation does not hold.

Of some interest is the CO-transfer reaction which leads to the formation of complexes of type (I). This is no doubt facilitated by the presence of an excess of $Fe_2(CO)_9$ in the reaction mixture, with its tendency to combine with phosphine ligands. From most of the reactions described, $Fe(CO)_4L$ and/or $Fe(CO)_3L_2$ complexes were also isolated. When chelating ligands, *e.g.* diphos or diars, were used, these ligand-transfer reactions did not occur, although since the platinum-containing precursor was $Pt(L_2)_2$ in both cases, it was not surprising to find $Fe(CO)_3L_2$ as one of the products. As expected, under these conditions complexes of type (I) were only formed with the less basic, and hence less strongly co-ordinated, phosphines, whereas those of type (II) predominated with the more strongly bonded ligands. Only in the case of (III) was any cluster complex isolated in which the phosphorus ligand had transferred to iron.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer. ^1H N.m.r. spectra were obtained with a Varian HA100 spectrometer. Mass spectra were obtained with an AEI MS 902 double-focusing mass spectrometer.

All reactions were carried out under nitrogen. Light petroleum had b.p. 40—60°. Chromatography was performed on Florisil columns initially made up in light petroleum. All solvents were dried and distilled before use. Analytical data, melting points, *etc.* are collected in Table 1.

The low-valent platinum complexes were made by literature methods, or by modifications thereof. Thus PtL_4 [$L = PPh_3$, PPh_2Me, $P(OPh)_3$, or $AsPh_3$; L_2 = diphos] were prepared from K_2PtCl_4, the appropriate ligand L, and $NaBH_4$ in aqueous ethanol.[13] The complexes PtL_4 [L =

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* Recently confirmed by single-crystal *X*-ray diffraction; R. Mason, J. Zubieta, A. T. T. Hsieh, J. Knight, and M. J. Mays, *J.C.S. Chem. Comm.*, 1972, 200.

[11] M. J. Church and M. J. Mays, *J. Inorg. Nuclear Chem.*, 1971, **33**, 253.

[12] J. J. Levison and S. D. Robinson, *J. Chem. Soc.* (*A*), 1970, 639.

[13] D. T. Rosevear and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 164.

$PPhMe_2$,* or $PPh(OMe)_2$, L_2 = diars] have not been previously reported. The following preparation exemplifies the method.

Preparation of Tetrakis(dimethyl phenylphosphonite)platinum(0), $Pt[PPh(OMe)_2]_4$.—A solution of potassium chloroplatinite (1·0 g) in water (10 ml) was added to a solution of dimethyl phenylphosphonite (1·64 g) in ethanol (4 ml) followed after 1 min by a solution of sodium borohydride (0·5 g) in water (10 ml). There was instant effervescence and a pale yellow oily solid was precipitated. Water (25 ml) was added and the mixture was stirred for 30 min. The aqueous ethanol was removed and the solid washed separately with water and ethanol, and then dried *in vacuo* to give the product as a pale yellow solid (95%).

Reactions between Enneacarbonyldi-iron(0) *and* [PtL_4] *Complexes*.— (a) *Tetrakis(diphenylmethylphosphine)platinum*(0). Enneacarbonyldi-iron(0) (0·8 g, 2·2 mmol) was added to the deep yellow solution of tetrakis(diphenylmethylphosphine)platinum(0) (0·96 g, 0·965 mmol) in benzene (20 ml) and the mixture was stirred. After 17 h the resultant deep red solution was evaporated (reduced pressure) to *ca*. 5 ml and chromatographed. Elution with light petroleum gave [$Fe(CO)_4(PMePh_2)$] and *trans*-[$Fe(CO)_3(PMePh_2)_2$], identified by their i.r. spectra. Further elution with 1 : 1 diethyl ether–light petroleum gave $Fe_2Pt(CO)_8(PMePh_2)_2$ (II; L = $PMePh_2$) which was recrystallised from diethyl ether–light petroleum to give the *product* as prisms. This complex was also prepared (14% yield) from the reaction of tetrakis(diphenylmethylphosphine)platinum(0) with dodecacarbonyltri-iron(0) in benzene.

(b) *Tetrakis(dimethylphenylphosphine)platinum*(0). Enneacarbonyldi-iron(0) (0·965 g, 2·65 mmol) was added to a solution of tetrakis(dimethylphenylphosphine)platinum(0) (0·99 g, 1·32 mmol) in benzene (20 ml) and the mixture was stirred for 20 h. The solution was evaporated to small volume (*ca*. 5 ml) and chromatographed. Elution with 1 : 49 diethyl ether–light petroleum gave [$Fe(CO)_4(PMe_2Ph)$] identified by its i.r. spectrum. Elution with 1 : 9 diethyl ether–light petroleum gave a red solution which was shown by i.r. to contain the species $Fe_2Pt(CO)_9(PMe_2Ph)$. Further elution with diethyl ether gave $Fe_2Pt(CO)_8(PMe_2Ph)_2$ which recrystallised from diethyl ether–light petroleum as *prisms*. Attempted purification of $Fe_2Pt(CO)_9(PMe_2Ph)$ by further chromatography gave only $Fe_2Pt(CO)_8(PMe_2Ph)_2$.

(c) *Tetrakis(dimethyl phenylphosphonite)platinum*(0). A mixture of enneacarbonyldi-iron(0) (2·0 g, 5·5 mmol) and tetrakis(dimethyl phenylphosphonite)platinum(0) (2·06 g, 2·35 mmol) in 1 : 1 benzene–tetrahydrofuran (40 ml) was stirred for 17 h. The red solution was reduced in volume (*ca*. 5 ml) and chromatographed. Elution with light petroleum gave $Fe(CO)_4[PPh(OMe)_2]$ and a trace of *trans*-[$Fe(CO)_3\{PPh(OMe)_2\}_2$] identified by their characteristic i.r. spectra. Elution with 1 : 1 diethyl ether–light petroleum gave $Fe_2Pt(CO)_8[PPh(OMe)_2]_2$ which recrystallised from diethyl ether–light petroleum as *prisms*.

(d) *Tetrakis(triphenyl phosphite)platinum*(0). Enneacarbonyldi-iron(0) (0·9 g, 2·25 mmol) was added to a solution of tetrakis(triphenyl phosphite)platinum(0) (1·21 g, 0·84 mmol) in benzene (25 ml) and tetrahydrofuran (15 ml) and the mixture was stirred for 19 h. The solution was evaporated (to *ca*. 5 ml) under reduced pressure and chromatographed. Elution with light petroleum gave $Fe(CO)_4[P(OPh)_3]$ and *trans*-[$Fe(CO)_3\{P(OPh)_3\}_2$] which were identified by their i.r. spectra. Elution with 1 : 9 diethyl ether–light petroleum gave $Fe_2Pt(CO)_8[P(OPh)_3]_2$ which recrystallised from diethyl ether–light petroleum as *prisms*. Further elution with 1 : 9 diethyl ether–light petroleum gave the complex thought to be [$FePt_2(CO)_5\{P(OPh)_3\}_3$] (III); this crystallised from diethyl ether–light petroleum as *prisms*.

(e) *Bis[bis(diphenylphosphino)ethane]platinum*(0). A mixture of enneacarbonyldi-iron(0) (0·72 g, 1·98 mmol) and bis[bis(diphenylphosphino)ethane]platinum(0) (1·13 g, 1·15 mmol) in benzene (50 ml) was stirred for 40 h. The solution was evaporated (*ca*. 5 ml) under reduced pressure and chromatographed. Elution with 2 : 1 diethyl ether–light petroleum gave $Fe_2Pt(CO)_8$(diphos), recrystallised from diethyl ether–light petroleum as *prisms*.

(f) *Tetrakis(triphenylarsine)platinum*(0). Enneacarbonyldi-iron(0) (0·2 g, 0·55 mmol) was added to a suspension of tetrakis(triphenylarsine)platinum(0) (0·38 g, 0·27 mmol) in benzene (15 ml) and the mixture was stirred for 4 h. The resultant deep red solution was evaporated to dryness, the residue extracted with light petroleum, and the extract chromatographed. Elution with light petroleum gave respectively $Fe(CO)_4AsPh_3$ (identified by its i.r. spectrum) and the presumed $Fe_2Pt(CO)_9(AsPh_3)$ which was recrystallised from light petroleum at −10° to give the product as deep red *prisms* (5 mg), m.p. 128—130°. This compound was characterised only by its i.r. spectrum.

(g) *Bis*[o-*phenylenebis(dimethylarsine)*]*platinum*(0). A mixture of enneacarbonyldi-iron(0) (1·0 g, 2·75 mmol) and bis[*o*-phenylenebis(dimethylarsine)]platinum(0) (0·92 g, 1·2 mmol) in benzene (35 ml) was stirred for 3 days and the mixture chromatographed. Elution with 1 : 19 diethyl ether–light petroleum and 1 : 9 diethyl ether–light petroleum gave *o*-$C_6H_4[AsMe_2Fe(CO)_4]_2$ and *o*-$C_6H_4(AsMe_2)_2Fe(CO)_3$, characterised from their i.r. spectra.[14] Further elution with 1 : 1 diethyl ether–light petroleum gave $Fe_2Pt(CO)_8$(diars), which crystallised from diethyl ether–light petroleum as *prisms*.

Reaction of Enneacarbonyldi-iron(0) *and Bis(triphenylphosphine)*(trans-*stilbene*)*platinum*(0).— Enneacarbonyldi-iron(0) (0·6 g, 1·65 mmol) was added to a well-stirred solution of bis(triphenylphosphine)(*trans*-stilbene)platinum(0) (0·7 g, 0·78 mmol) in benzene (20 ml). A deep red colour appeared after 5 min. After 20 h the solution was evaporated to dryness under reduced pressure and the resulting oil was extracted with light petroleum (50 ml) and the extract chromatographed. Elution with light petroleum gave separately *trans*-stilbene, $Fe(CO)_4PPh_3$, $Fe(CO)_3(PPh_3)_2$, and $Fe_2Pt(CO)_9(PPh_3)$. The latter was recrystallised from warm light petroleum to give the product as *prisms*.

Reaction between Dodecacarbonyltri-iron(0) *and Bis(triphenylphosphine)*(trans-*stilbene*)*platinum*(0).—A mixture of dodecacarbonyltri-iron(0) (0·5 g, 1·0 mmol) and bis(triphenylphosphine)(*trans*-stilbene)platinum(0) (0·9 g, 1·0 mmol) dissolved in benzene (20 ml) was stirred for 2 days, and chromatographed. Elution with 1 : 9 diethyl ether–light petroleum gave $Fe_2Pt(CO)_9(PPh_3)$ in 10% yield. Elution with 1 : 1 diethyl ether–light petroleum gave

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* The preparation of $Pt(PPhMe_2)_4$ was reported while this paper was being written (H. C. Clark and K. Itoh, *Inorg. Chem.*, 1971, **10**, 1707).

[14] W. R. Cullen and D. A. Harbourne, *Canad. J. Chem.*, 1969, **47**, 3371.

$Fe_2Pt(CO)_8(PPh_3)_2$. Further elution with 7 : 3 diethyl ether–light petroleum gave separately $[Pt_4(CO)_6(PPh_3)_3]$ as an amorphous powder, m.p. 136—140° (dec.), from benzene–light petroleum [Found: C, 41·6; H, 2·95; O, 5·4; P, 5·5; Pt, 44·6%; *M* (osmometric in chloroform), 1680. $C_{60}H_{45}O_6P_3Pt_4$ requires C, 41·6; H, 2·6; O, 5·6; P, 5·4; Pt, 44·9%; *M*, 1735], ν(CO) 2025s, 2004s, 1994s, 1941m, 1893m, 1857m, 1817sh, and 1788s cm^{-1}; and $Pt_4(CO)_8(PPh_3)_3$ as *prisms*, m.p. >146° (dec.), from benzene–light petroleum [Found: C, 41·8; H, 2·6; O, 6·7; P, 5·9; Pt, 42·8%; *M*, 1788. $C_{62}H_{45}O_8P_3Pt_4$ requires C, 41·6; H, 2·6; O, 7·2; P, 5·2; Pt, 43·6%; *M*, 1791], ν(CO) 2025s, 2007sh, 1993, 1940m, 1893m, 1857m, and 1789s cm^{-1}. These complexes were obtained in 16 and 8% yields, respectively.

Reaction of Enneacarbonyldi-iron(0) *with* cis-*Dichlorobis*(*trimethylphosphine*)*platinum*(II).— Enneacarbonyldi-iron(0) (2·1 g, 5·75 mmol) was added to a solution of *cis*-dichlorobis(trimethylphosphine)platinum(II) (0·8 g, 1·95 mmol) in benzene (30 ml) and tetrahydrofuran (20 ml), and the mixture was stirred for 3 days. The solution was evaporated to dryness under reduced pressure, and the residue dissolved in benzene (6 ml) and chromatographed. Elution with 1 : 19 diethyl ether–light petroleum gave $[Fe(CO)_4(PMe_3)]$ followed by $Fe_2Pt(CO)_9(PMe_3)$. The latter was recrystallised from diethyl ether–light petroleum to give the product as red prisms, m.p. 92—94° (dec.) (3% yield), which quickly decomposed when set aside. Further elution with diethyl ether gave $Fe_2Pt(CO)_8(PMe_3)_2$, which crystallised from diethyl ether–light petroleum as *prisms*.

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